

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-109635

(43)Date of publication of application : 23.04.1999

(51)Int.Cl.

G03F 7/075

G03F 7/022

G03F 7/037

H01L 21/027

(21)Application number : 09-286252

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(22)Date of filing : 03.10.1997

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## (54) PHOTSENSITIVE POLYAMIDE RESIN COMPOSITION

(57)Abstract:

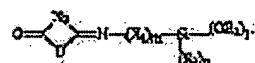
PROBLEM TO BE SOLVED: To obtain a positive photosensitive resin compsn. capable of giving a pattern having high adhesion and excellent in resolution at the time of development and forming a film having satisfactory waterproofing adhesive property to a substrate after heat treatment by using a specified polyamide, naphthoquinone diazide and a specified adhesive as essential components.

SOLUTION: The photosensitive resin compsn. contains 100 pts.wt. polyamide contg. repeating units of formula I, 0.5-40 pts.wt. naphthoquinone diazide and 0.05-20 pts.wt. adhesive of formula II and/or formula III as essential components. In the formula I each of X1 and X2 is a divalent arom. group. In the formulae II, III, X4 is

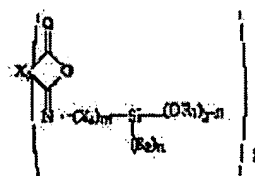
a divalent org. group contg. C directly bonded to Si, (m) is an integer of 0 or 1, each of R1 and R2 is 1-4C alkyl, (n) is an integer of 0, 1 or 2, X, is divalent hydrocarbon having bonding radicals to adjacent C atoms or the like, X5 is a group of formula IV and X6 is -O-, -CO- or the like. The components are dissolved in a solvent and used in the state of varnish.



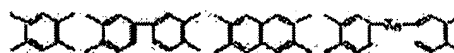
I



II



III



IV

## LEGAL STATUS

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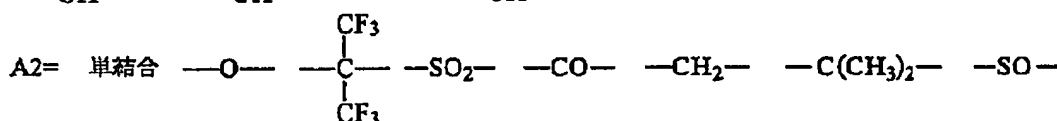
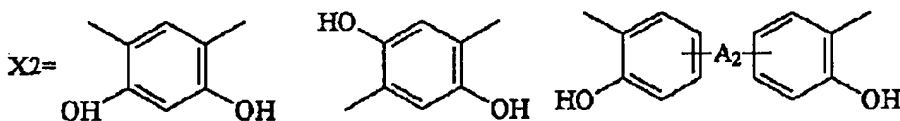
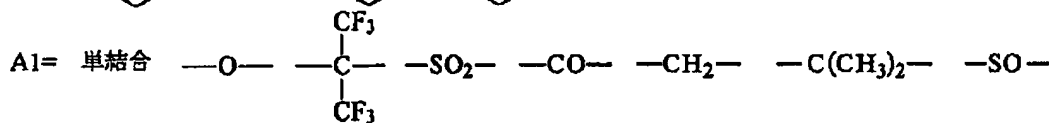
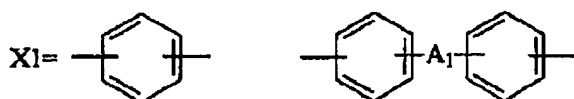
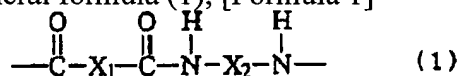
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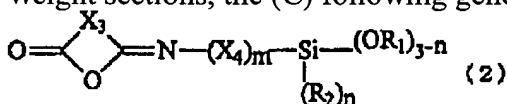
## CLAIMS

[Claim(s)]

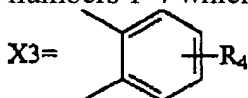
[Claim 1] (A) The polyamide 100 weight section including a repeat unit expressed with the following general formula (1), [Formula 1]



(B) The adhesives 0.05 - 20 weight sections which are expressed with naphthoquinonediazide 0.5 - 40 weight sections, the (C) following general formula (2), and/or (3), [Formula 2]

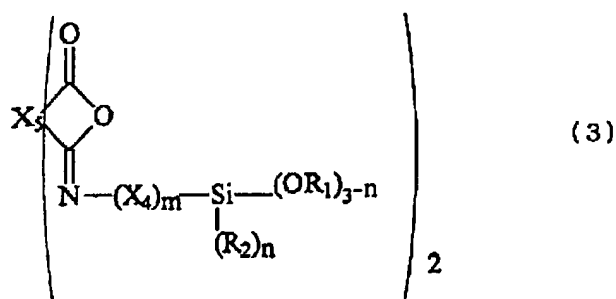


The divalent organic radical and m containing the carbon atom which couples X<sub>4</sub> directly with a silicon atom show among [type that the integer of 0 or 1, R<sub>1</sub>, and R<sub>2</sub> are the same, or the alkyl group of carbon numbers 1-4 which may differ, n is the integer of 0, 1, or 2, and X<sub>3</sub> is a formula. [Formula 3]

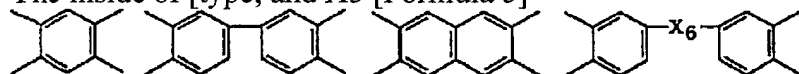


It is the divalent hydrocarbon group which has a joint radical in (the inside R<sub>4</sub> of a formula being an alkyl group or carboxyl group of a hydrogen atom and carbon numbers 1-4), or a contiguity carbon atom.]

[Formula 4]

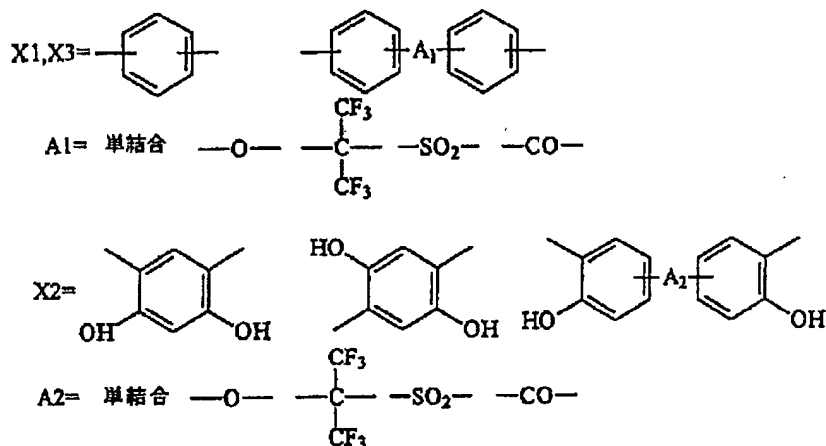
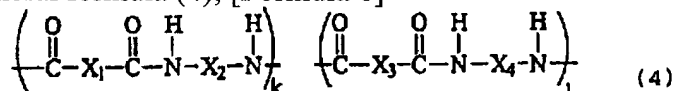


The inside of [type, and X5 [Formula 5]



An example and X6 It is -O-, -CO-, -S-, -SO<sub>2</sub>-, -CH<sub>2</sub>-, -C(CH<sub>3</sub>)<sub>2</sub>-, or -C(CF<sub>3</sub>)<sub>2</sub>-, and the above X<sub>4</sub>, R<sub>1</sub>, R<sub>2</sub>, and n and m are the same as the above.] The photopolymer constituent characterized by becoming as an indispensable component.

[Claim 2] (A) The polyamide 100 weight section including a repeat unit expressed with the following general formula (4), [Formula 6]



X4 = the divalent aromatic series radical X1 and X3 Mutually-independent k and l express a mole fraction.  $k+l=100$  mol %  $60 \leq k \leq 100$ , naphthoquinonediazide 0.5 given in 40  $\geq l > 0$  (B) claim 1 - 40 weight sections, (C) Photopolymer constituent characterized by becoming considering the adhesives 0.05 - 20 weight sections which are expressed with a general formula (2) and/or (3) according to claim 1 as an indispensable component.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the positive type photopolymer presentation which is high adhesion and can obtain a good pattern at the time of development.

[0002]

[Description of the Prior Art] Conventionally, the polyimide resin having the outstanding thermal resistance, an electrical property, a mechanical characteristic, etc. is used for the surface-protection film of a semiconductor device, and the interlayer insulation film. However, while high integration of a semiconductor device and enlargement progress in recent years, there is a demand of thin-shape-izing of a closure resin package and a miniaturization, methods, such as LOC (lead-on chip) and a surface mount by the solder reflow, are adopted, and the polyimide resin which was excellent in a mechanical characteristic, thermal resistance, etc. more than the former has come to be needed. Although it has the feature that a pattern creation process can be simplified if this is used, and a complicated manufacturing process can be shortened on the other hand although the photosensitive polyimide resin which gave photosensitive ability to polyimide resin itself has been used, since organic solvents, such as a N-methyl-2-pyrrolidone, are needed in the case of development, a technical problem remains from the point of safety and an environmental problem. Then, research of the photopolymer of the positive type which can do development in an alkali aqueous solution is made recently. For example, the positive type photopolymer which consists of poly benzo oxazole resin and a diazo quinone compound is indicated by JP,1-46862,B and JP,8-269198,A. This has the outstanding thermal resistance, an electrical property, and micro-processing nature, and has not only a wafer coat use but the applicability as resin for layer insulation. However, since this photosensitive poly benzo oxazole resin was inferior to adhesion with a substrate, especially a silicon wafer, in order to have the serious defect in which resin exfoliates from a substrate, the time of development, or after heat curing and to have used this positive type photosensitivity poly benzo oxazole resin in the actual process, the treatment which applies adhesives beforehand is required for a substrate, and there was a problem to which a process becomes complicated.

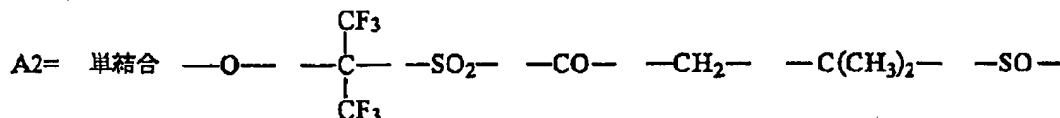
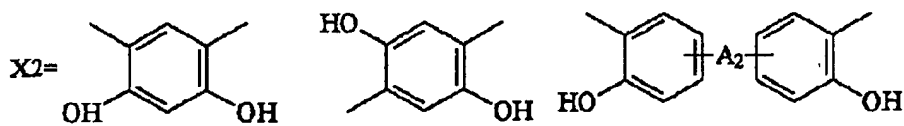
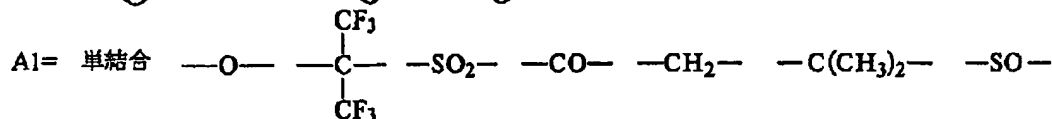
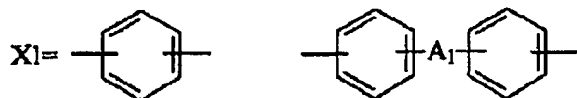
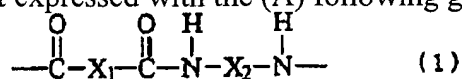
[0003] Although the polyimide resin which contains silicon in that structure to poly benzo oxazole resin in JP,7-281441,A as a method of solving this problem is added and adhesion with a substrate is taken out, the waterproof adhesive property is inferior in this polyimide resin, there is a limit in that activity in respect of reliability, and a large system of an activity range is desired rather than many for the problem.

[0004]

[Problem(s) to be Solved by the Invention] This invention is to be able to obtain the pattern which was excellent in resolution with high adhesion at the time of development, and for the film after the heat treatment offer the good positive type photopolymer constituent of a waterproof adhesive property to a substrate.

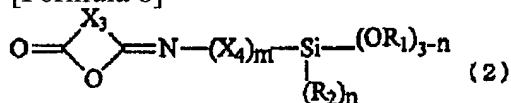
[0005]

[Means for Solving the Problem] This invention is the polyamide 100 weight section including a repeat unit expressed with the (A) following general formula (1), [Formula 7]

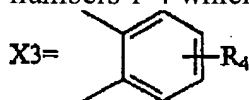


(B) The adhesives 0.05 - 20 weight sections which are expressed with naphthoquinonediazide 0.5 - 40 weight sections, the (C) following general formula (2), and/or (3), [0006]

[Formula 8]



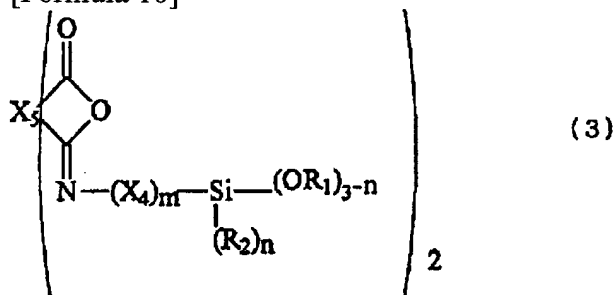
The divalent organic radical and m containing the carbon atom which couples X4 directly with a silicon atom show among [type that the integer of 0 or 1, R1, and R2 are the same, or the alkyl group of carbon numbers 1-4 which may differ, n is the integer of 0, 1, or 2, and X3 is a formula. [Formula 9]



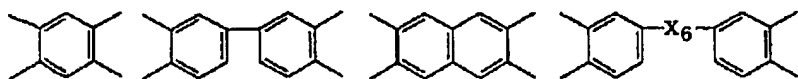
It is the divalent hydrocarbon group which has a joint radical in (the inside R4 of a formula being an alkyl group or carboxyl group of a hydrogen atom and carbon numbers 1-4), or a contiguity carbon atom.]

[0007]

[Formula 10]

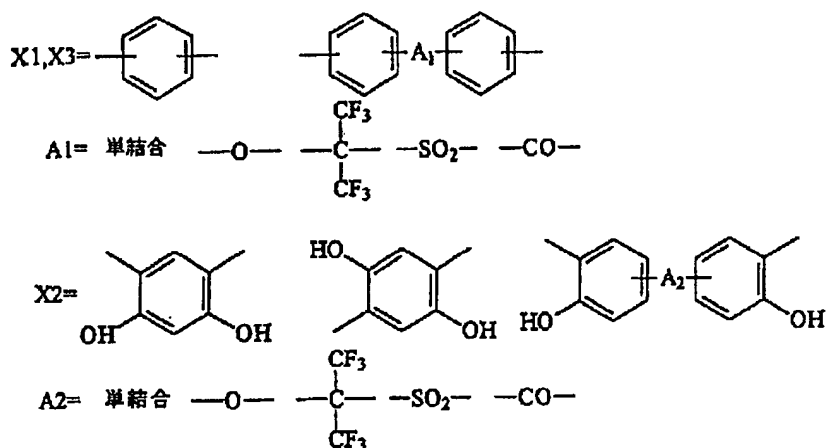
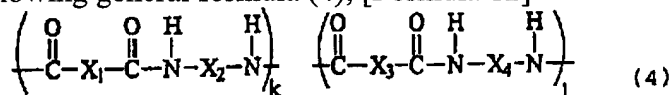


The inside of [type, and X5 [Formula 11]



An example and X6 It is -O-, -CO-, -S-, -SO<sub>2</sub>-, -CH<sub>2</sub>-, -C(CH<sub>3</sub>)<sub>2</sub>-, or -C(CF<sub>3</sub>)<sub>2</sub>-, and the above X4, R1, R2, and n and m are the same as the above.] It is the photopolymer constituent characterized by becoming as an indispensable component.

[0008] Moreover, the polyamide 100 weight section including the repeat unit expressed with the (A) following general formula (4), [Formula 12]



X4 = the divalent aromatic series radical X1 and X3 Mutually-independent k and l express a mole fraction, and are k+l=100 mol %60 <=k<100 and 40>=l>0. [0009] (B) It is the photopolymer constituent characterized by becoming considering the adhesives 0.05 - 20 weight sections which are expressed with the aforementioned naphthoquinonediazide 0.5 - 40 weight sections, the general formula (2) of (C) above, and/or (3) as an indispensable component. A polyamide (A) can be obtained here by dihydroxy diamine, the method of making it condense, and the method of condensing dicarboxylic acid and dihydroxy diamine with condensing agents, such as dicyclohexylcarbodiimide, by forming into acid chloride the method of acquiring to JP,64-6947,A, JP,60-223824,A, JP,63-96162,A, etc. by the condensation of the dicarboxylic acid chloride and dihydroxy diamine which are the method of a publication, and dicarboxylic acid using a thionyl chloride etc.

[0010] As corresponding dicarboxylic acid, the derivatives, such as a - dicarboxy benzophenone, and - diphenyl sulfone dicarboxylic acid, and phthalic-acid, isophthalic acid, terephthalic-acid, 4, and 4'-diphenyl ether dicarboxylic acid, 4, and 4'-2, 2'-screw (4-carboxyphenyl) hexafluoropropane, 4, and 4'-4, 4'-dicarboxy biphenyl, are mentioned. As diamine, moreover, 1, 5-dihydroxy -2, 4-diaminobenzene, 1, 4-dihydroxy -2, 5-diaminobenzene, 3, the 3'-diamino -4, a 4'-dihydroxy benzophenone, 4, the 4'-diamino -3, a 3'-dihydroxy benzophenone, screw (3-amino-4-hydroxyphenyl)-hexafluoropropane, Screw (4-amino-3-hydroxyphenyl)-hexafluoropropane, 3, the 3'-diamino -4, a 4'-dihydroxy biphenyl, 4, the 4'-diamino -3, a 3'-dihydroxy biphenyl, 3, the 3'-diamino -4, 4'-dihydroxy phenyl ether, 4, the 4'-diamino -3, 3'-dihydroxy phenyl ether, 3, the 3'-diamino -4, 4'-dihydroxy phenyl sulfoxide, 4, the 4'-diamino -3, 3'-dihydroxy phenyl sulfoxide, 3, the 3'-diamino -4, 4'-dihydroxy phenyl sulfone, 4, the 4'-diamino -3, 3'-dihydroxy phenyl sulfone, 3 and 3'-diamino -4 and 4 - dihydroxy phenylmethane, and '4, 4' -- the - diamino -3 and 3' -- the compound which has hydroxyl in intramoleculars, such as - dihydroxy phenylmethane and its derivative, is mentioned.

[0011] As a diamine component, although an activity can do hydroxy diamine independently, divalent aromatic series diamine can also be added in part as a component of diamine in order to adjust the

solubility of a constituent. The method of adding two or more kinds of diamines simultaneously as a method of adding and the method of adding independently may be used. As this diamine, it is a -diamino diphenyl sulfone, and -diamino benzophenone, and -diamino diphenyl ether, and -diamino diphenyl ether, and o-phenylenediamine, m-phenylenediamine, p-phenylene diamine, 4, and 4'3, 4'-diamino diphenyl ether, 3, and 3'4, 4'-diamino biphenyl, 4, and 4'4, 4'-diamino diphenyl sulfone, 3, and 3'4, 4'-diamino diphenyl sulfide, [0012] 4, 4'-diamino diphenylmethane, 4, the 4'-diamino -3, 3'-dimethyl diphenylmethane, -diamino -3, 3', and 4 and 4'5, 5'-tetramethyl diphenylmethane, A 4 and 4'-diamino benzanilide, 1, 5-diamino naphthalene, 3, 3'-dimethoxy -4, a 4'-diamino biphenyl, 3, the 3'-dimethyl -4, a 4'-diamino biphenyl, 1, 4-screw (4-amino phenoxy) benzene, 1, 3-screw (4-amino phenoxy) benzene, 2 and 2-screw [(a 4-(4-amino phenoxy) phenyl) propane --) screw [(4-(4-amino phenoxy) phenyl) sulfone, screw [(4-(3-amino phenoxy) phenyl) sulfone --)) Screw [(4-(4-amino phenoxy) phenyl) ether, 4, and 4'-screw (4-amino phenoxy) biphenyl, 2, and 2-screw [(4-(4-amino phenoxy) phenyl) hexafluoropropane etc. is mentioned.)) If the ratio of divalent diamine exceeds 40% by the mole ratio, since the patterning nature of a constituent will fall, it is not desirable.

[0013] Next, the derivative of the various naphthoquinonediazide used with the gestalt mixed to the novolak resin which is the principal component of the positive resist currently widely used as a present semiconductor resist can be used for naphthoquinonediazide (B). This naphthoquinonediazide can be obtained as follows, for example.

[0014] It is made to react under existence of basic catalysts, such as triethylamine, into solvents, such as ballast, such as alcohol or a phenol derivative, a TETORAHIDO furan, or dioxane, and it esterifies and the derivative of diazo naphthoquinone-5-sulfonic-acid chloride or diazo naphthoquinone-4-sulfonic-acid chloride is obtained. Various compounds can be used as a compound of the ballast in that case. For example, polyhydroxy benzophenones, such as a hydroxy benzophenone and a dihydroxy benzophenone, Polyhydroxy biphenyls, such as a 4-hydroxy biphenyl, 4, and 4'-hydroxy biphenyl, A phenol, cresol, a xylenol, a naphthol, a 2-phenyl-2-(4-hydroxyphenyl) propane, 2 and 2-screw (4-hydroxyphenyl) propane, the 1-phenyl -1, 1-screw (4-hydroxyphenyl) ethane, A hydroquinone, a pyrocatechol, resorcinol, pyrogallol, a phloroglucinol, Bisphenol A, a p-cresol trimer, 3 and 4, 5-trihydroxy benzoic-acid methyl ester, 3, 4, 5-trihydroxy benzoic-acid propyl ester, 1-acetyl - 2, 3, 4-trihydroxy benzene, 1-acetyl - 2, 4, 6-trihydroxy benzene, a tetra-hydroxy Spirobi sault indan, They are -tetra-hydroxy diphenyl sulfide, 2, 2', and hexa hydroxy Spirobi sault indan, 2, 2', 4, and 4'4, 4'-tetra-hydroxy diphenyl sulfoxides, these derivatives, etc. Moreover, in this reaction, the rate of esterification is controllable by adjusting the mole ratio of the sulfonic-acid chloride of a diazo naphthoquinone, and ballast.

[0015] In this invention, if there are few amounts of the diazo naphthoquinone to be used to the polyamide resin 100 weight section than the 0.5 weight section, patterning nature will fall remarkably, and the machine physical properties of the film which heat-treated the relief pattern after patterning when 40 weight sections were exceeded fall remarkably, and it is not desirable.

[0016] Adhesives (C) are obtained as follows. First, the derivative etc. and silicon amine of the anhydride of dicarboxylic acid or two anhydrides of tetracarboxylic acid can be made to be able to act in solvents, such as N-methyl pyrrolidone, and then this solution can be obtained by making condensing agents, such as dicyclohexylcarbodiimide, act. Various structures can use a carboxylic anhydride here, for example, pyromellitic dianhydride and benzophenone tetracarboxylic acid 2 anhydride, biphenyl tetracarboxylic acid 2 anhydride, oxy-JIFUTARU acid 2 anhydride, diphenylsulfone tetracarboxylic acid 2 anhydride, diphenyl hexafluoro propylidene tetracarboxylic acid 2 anhydride, trimellitic acid anhydride, phthalic anhydride, and cyclobutane tetracarboxylic acid 2 anhydride, cyclopentane tetracarboxylic acid 2 anhydride, terphenyl tetracarboxylic acid 2 anhydride, etc. are mentioned.

[0017] The various structures of a silicon amine are also usable, for example, aminoethyl trimethoxysilane, aminoethyl triethoxysilane, aminopropyl trimethoxysilane, aminopropyl triethoxysilane, cyclohexylamino propyltrimethoxysilane, piperazino propyltrimethoxysilane, etc. are mentioned. In this invention, it is the range of 0.05 - 20 weight section, to the polyamide resin 100 weight section, if there are few adhesives than the 0.05 weight section, a substrate adhesive property will



fall, the problem which deposits out of a constituent if there are more amounts than 20 weight sections arises, and the amount of adhesives is not desirable.

[0018] These components are used for a solvent by making it the shape of a varnish, dissolving in this invention. As a solvent which can be used here, a N-methyl-2-pyrrolidone, gamma-butyrolactone, N,N-dimethylacetamide, dimethyl sulfoxide, diethylene-glycol diethylether, Diethylene-glycol dibutyl ether, propylene glycol monomethyl ether, Dipropylene glycol monomethyl ether, propylene-glycol-monomethyl-ether acetate, Methyl lactate, ethyl lactate, butyl lactate, methyl -1, 3-butylene-glycol acetate, 1, the 3-butylene-glycol-3-monomethyl ether, methyl pyruvate, pyruvic-acid ethyl, methyl-3-methoxy propionate, etc. are mentioned, and these are independent -- or it can be mixed and used.

[0019] The photopolymer constituent of this invention is used as follows. Spreading by revolution spreading and the roll coater which used the spinner for the suitable substrate, for example, a silicon wafer, for this constituent is performed. This is dried at 50-130 degrees C using oven or a hot plate, and chemical rays are irradiated through a mask using a contact aligner or a stepper. The rinse by the rinse which carries out dissolution clearance of the exposure section with a developer here, and continues is performed, and the relief pattern of a wish is obtained.

[0020] As a developer, the aqueous solution of inorganic alkali salt, such as a sodium hydroxide and sodium bicarbonate, Tetramethylammonium hydroxide, tetraethylammonium hydroxide, Trimethylhydroxyethylammonium hydroxide, monomethylamine, Dimethylamine, a trimethylamine, a monoethyl amine, diethylamine, The aqueous solution of organic alkali, such as triethylamine, mono-isopropylamine, diisopropylamine, and ethanolamine or the organic solvent of specification [ this ], for example, alcohol, (for example, a methanol --) the averages, such as ethanol, -- a surfactant (for example, alkyl naphthalene sulfonic-acid sodium --) The aqueous solution which added alkyl benzene sodium sulfonate, lauryl sulfonic-acid sodium, an alkyl naphthalene sulfonic acid, a lauryl sulfonic acid, alkylbenzene sulfonic acid, etc. if needed can be used.

[0021] The development method is developed with a spray, a paddle, a DIP method, etc. A rinse can use distilled water, deionized water, etc. This relief pattern is heat-treated in oven etc., and it becomes the last film by oxazole-izing. It is desirable to process from 30 minutes at the temperature of 300-450 degrees C under a nitrogen air current or an air air current as conditions for heat-treatment for about several hours.

[0022]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained to details.

[The example 1 of reference]: A thionyl chloride (0.63 mols, 75.0g) is dropped at 1l. separable flask of composition of polymer at a room temperature at isophthalic acid (0.27 mols, 44.9g) and the N,N-dimethylacetamide (600g) solution of N and N-dimethylamino pyridine (0.03 mols, 3.7g), and agitate for 1 hour. To 1l. separable flask, this solution is added at 0 degree C, and is agitated under a room temperature for 6 hours at the solution of the N,N-dimethylacetamide (300g) of 2 and 2-screw (3-amino-4-hydroxyphenyl)-hexafluoropropane (0.30 mols, 109.9g). Phthalic anhydride (0.06 mols, 8.9g) is added to this solution, and it agitates for further 10 hours. This was diluted with N,N-dimethylacetamide (1000g), and it was dropped, agitating in water, water was removed, the vacuum drying was carried out at 40 degrees C, and polymer (P-1) was obtained. It was  $\eta_{sp}/c=0.40$  when the reduced viscosity of the 1%N-methyl pyrrolidone solution of this polymer was measured.

[Examples 2-5 of reference] As shown in a table 1 below, aromatic carboxylic acid and aromatic series diamine were changed, and polymer was compounded like the example 1 of reference.

[0023]

[A table 1]

表 1

ポリマー No.	ジカルボン酸 モル、g	ジアミン モル、g	$\eta$ sp
P-1	イソフタル酸 0.27モル、44.9g	2, 2-ビス (3-ア ミノ-4-ヒドロキ シフェニル)-ヘキサ フルオロプロパン 0.30モル、109.9g	0.40
P-2	イソフタル酸 0.135モル、22.4g 4, 4'-ジフェニ ルエーテルジカルボ ン酸 0.135モル、34.9g	2, 2-ビス (3-ア ミノ-4-ヒドロキ シフェニル)-ヘキサ フルオロプロパン 0.27モル、98.9g 4, 4'-ジアミノジ フェニルエーテル 0.03モル、6.0g	0.45
P-3	4, 4'-ジフェニ ルエーテルジカルボ ン酸 0.27モル、69.7g	2, 2-ビス (3-ア ミノ-4-ヒドロキ シフェニル)-ヘキサ フルオロプロパン 0.30モル、109.9g	0.30
P-4	2, 2'-ビス (4 -カルボキシフェニ ル)-ヘキサフルオロ プロパン 0.27モル、105.9g	2, 2-ビス (3-ア ミノ-4-ヒドロキ シフェニル)-ヘキサ フルオロプロパン 0.30モル、109.9g	0.30
P-5	2, 2'-ビス (4 -カルボキシフェニ ル)-ヘキサフルオロ プロパン 0.27モル、105.9g	3, 3'-ジヒドロキ シ-4, 4'-ジアミ ノビフェニル 0.30モル、64.9g	0.44

[0024] [The example 6 of reference]: Dissolve the composition 2 and 3 of naphthoquinonediazide, 4-trihydroxy benzophenone (0.1 mols, 23.0g), and 1 and 2-naphthoquinonediazide-5-sulfonic acid chloride (0.3 mols, 80.6g) in a tetrahydrofuran (500g), and triethylamine (0.3 mols, 30.4g) is dropped, and agitate at a room temperature for 15 hours. The sludge was filtered, and it was dropped, agitating a solution in water, the vacuum drying of the water was removed and carried out, and it considered as naphthoquinonediazide A-1.

[Examples 7 and 8 of reference] As shown in a table below, the compound of naphthoquinone sulfonic acid chloride and a phenol was changed, naphthoquinonediazide was compounded like the example 6 of reference, and naphthoquinonediazide A-2 and A-3 were obtained.

[0025]

[A table 2]

表 2

参考例	No.	ナフトキノン部位	バラスト化合物
6	A-1	1, 2-ナフトキノンジアジド-5-スルホン酸クロリド (0. 3モル、80. 6 g)	2, 3, 4-トリヒドロキシベンゾフェノン (0. 1モル、23. 0 g)
7	A-2	1, 2-ナフトキノンジアジド-4-スルホン酸クロリド (0. 2モル、53. 7 g)	1, 1 -ビス (4-ヒドロキシフェニル) -1-フェニルエタン (0. 1モル、29. 0 g)
8	A-3	1, 2-ナフトキノンジアジド-5-スルホン酸クロリド (0. 1モル、28. 9 g)	2-フェニル-2- (4-ヒドロキシフェニル) プロパン (0. 1モル、21. 2 g)

[0026] [The example 9 of reference]: N-methyl pyrrolidone (100g) solution of aminopropyl triethoxysilane (0.2 mols, 44.2g) was added to 1l. separable flask of adjustments of an adhesion assistant at 0 degree C at N-methyl pyrrolidone (164g) solution of pyromellitic acid 2 anhydride (0.1 mols, 21.8g). This is agitated at a room temperature for 4 hours. N-methyl pyrrolidone (40g) solution of dicyclohexylcarbodiimide (0.2 mols, 41.3g) is added to this solution as a condensing agent at 0 degree C, and it agitates at a room temperature for 4 hours. This is filtered using a filter and it considers as the solution (C-1) of an adhesion assistant. When the infrared absorption spectrum of this solution was measured, in the wave number of 1800cm<sup>-1</sup>, the absorption peak originating in iso imide was checked. [Examples 10-13 of reference] As shown in a table below, the acid anhydride and the amino siloxane compound were changed and the solution C-2 to C-5 of an adhesion assistant was adjusted like the example 9 of reference.

[0027]

[A table 3]

表3

参考例	No.	酸無水物	アミノシロキサン化合物
9	C-1	ピロメリット酸二無水物 (0.1モル、21.8g)	アミノプロピルトリエトキシシラン (0.2モル、44.2g)
10	C-2	ベンゾフェノンテトラカルボン酸二無水物 (0.1モル、32.2g)	アミノプロピルトリエトキシシラン (0.2モル、44.2g)
11	C-3	ジフェニルスルホンテトラカルボン酸二無水物 (0.1モル、36.8g)	アミノプロピルトリエトキシシラン (0.2モル、44.2g)
12	C-4	オキシジフタル酸二無水物 (0.1モル、31.0g)	アミノプロピルトリエトキシシラン (0.2モル、44.2g)
13	C-5	フタル酸二無水物 (0.1モル、14.8g)	アミノプロピルトリエトキシシラン (0.2モル、44.2g)

[0028] The developer A (presentation which consists of the tetramethylammonium hydroxide 2.3 weight section, the pure water 96.7 weight section, and the dodecylbenzenesulfonic acid 1.0 weight section) besides [ marketing ] NMD-3 (Tokyo adaptation shrine make) was used for the developer which [developer adjusted ] used.

[0029] (Example 1) The constituent of the polymer (P-1) 100 weight section, the PAC(A-1) 20 weight section, the adhesion assistant (C-1) 10 weight section (they are 2 weight sections at a pure part), and the NMP230 weight section is adjusted. Spin spreading of this constituent is carried out at a silicon wafer, it dries at oven 80 degree C for 20 minutes, and a 10-micron paint film is formed after spreading. Reticule with a test pattern is used for this, i line stepper (NIKON CORP. make) is used, and they are 500 mJ/cm<sup>2</sup>. When energy was irradiated and the rinse was carried out with water for 20 seconds after paddle development for 30 seconds per minute with the developer of NMD-3, the good pattern with a resolution [ without peeling of a pattern ] of 10 microns was obtained.

(Examples 2-6) The pattern of the result shown in a table 4 was obtained by the same actuation as an example 1 using the presentation of the component shown in a table 4.

[0030]

[A table 4]

表4

実施例	組成	露光エネルギー	現像条件	解像度
1	(P-1) 100 (A-1) 20 (C-1) 2 (純分) NMP 230	i線ステッパー 500 mJ	NMD-3 (1min30sec) 水 (リンス) (30sec)	8 $\mu$ m
2	(P-2) 100 (A-2) 20 (C-2) 2 (純分) NMP 250	i線ステッパー 600 mJ	NMD-3 (2min30sec) 水 (リンス) (30sec)	10 $\mu$ m
3	(P-3) 100 (A-3) 20 (C-2) 2 (純分) NMP 200	i線ステッパー 500 mJ	現像液A (1min30sec) 水 (リンス) (30sec)	8 $\mu$ m
4	(P-3) 100 (A-3) 20 (C-3) 2 (純分) NMP 200	i線ステッパー 500 mJ	現像液A (1min30sec) 水 (リンス) (30sec)	8 $\mu$ m
5	(P-4) 100 (A-3) 20 (C-4) 2 (純分) NMP 200	i線ステッパー 600 mJ	現像液A (1min30sec) 水 (リンス) (30sec)	8 $\mu$ m
6	(P-5) 100 (A-2) 20 (C-5) 2 (純分) NMP 230	i線ステッパー 500 mJ	NMD3 (1min30sec) 水 (リンス) (30sec)	8 $\mu$ m

[0031] (Example 7) By the same method as an example 1, without carrying out, after forming a paint film, using inert oven, the constituent used in the example 1 was heat-treated at 350 degrees C for 2 hours, and exposure and development used it as the film of poly benzoxazole. In 133 more degree-C two atmospheric pressures, it processes with a pressure cooker for 200 hours. When examined by tearing these off (the area which \*\*\*\* a film with a cutter knife so that 100 squares of 1mm may be located in a line, is made to stick 3 M company mending tape to this, tears off, and remains on a substrate estimates), the good result was obtained as shown in a table 5.

(Examples 8-12) When examined by processing the presentation of a publication to a table 5 and tearing off to it by the same method as an example 7, the good result was obtained as shown in a table 5.

[0032]

[A table 5]

表 5

実施例	組成	プレッシャークック カー0時間	プレッシャークック カー200時間
7	(P-1) 100 (A-1) 20 (C-1) 2 (純分) NMP230	100/100	100/100
8	(P-2) 100 (A-2) 20 (C-2) 2 (純分) NMP250	100/100	100/100
9	(P-3) 100 (A-3) 20 (C-2) 2 (純分) NMP200	100/100	100/100
10	(P-3) 100 (A-3) 20 (C-3) 2 (純分) NMP200	100/100	100/100
11	(P-4) 100 (A-3) 20 (C-4) 2 (純分) NMP200	100/100	100/100
12	(P-5) 100 (A-2) 20 (C-5) 2 (純分) NMP230	100/100	100/100

[0033] (Example 1 of a comparison) The constituent of the polymer (P-1) 100 weight section, the PAC (A-1) 20 weight section, and the NMP230 weight section is adjusted. When spreading, exposure, and development were performed by the same method as an example 1, the pattern exfoliated this constituent at the time of development.

(Example 2 of a comparison) When examined by tearing off by the method of indicating the above-mentioned constituent in the example 7, residual mark were not concerned with pressure cooker processing, but were 0/100.

[0034] (Example 3 of a comparison) They are benzophenone tetracarboxylic dianhydride 64.4g and 1 and 3-screw (3-aminopropyl) as silicon-containing polyimide resin. - 1, 1, 3, and 3-tetramethyl disiloxane 44.7g was dissolved in N-methyl pyrrolidone 400g, and it agitated at the room temperature overnight. It is dropped agitating this solution in water, water is removed, a vacuum drying is carried out at 40 degrees C, and it considers as polyimide precursor resin (PC-1). The constituent of the polymer (P-1) 100 weight section, the PAC(A-1) 20 weight section, the polyimide precursor resin (PC-1) 2 weight section, and the NMP230 weight section is adjusted. Although what has pressure cooker processing that a remaining point is nothing was 100/100 when examined by tearing off by the method of indicating this constituent in the example 21, what was processed was 0/100.

[0035]

[Effect of the Invention] By this invention, the pattern which was excellent in resolution with high adhesion at the time of development could be obtained, and the film after the heat treatment was able to offer the good positive type photopolymer constituent of a waterproof adhesive property to a substrate.

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[Translation done.]